hexoic acid being mainly obtained. This ketone has been obtained by carrying out the reaction with 0.1 mole of the anhydride in an equal volume of ethylene chloride. The mixture (saturated with boron fluoride) was stirred for four hours while cooled in a salt-ice slush, and then treated with sodium acetate. The solvent was distilled and the residue fractionated. However, when this modified procedure was used with 0.25 mole of the anhydride, the yield of ketone was very low, 2-ethylhexoic acid being mainly obtained.

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Bromo Derivatives of 1-Methyl-3-carbethoxy-4-piperidone

BY S. M. MCELVAIN AND JOHN C. SAFRANSKI, JR.

The bromination of 1-methyl-3-carbethoxy-4-piperidone (I) in carbon tetrachloride with one equivalent of bromine yields the hydrobromide of 1-methyl-3-carbethoxy-3-bromo-4-piperidone (II); with one-half an equivalent of bromine a mixture of the hydrobromides of I and II are precipitated and some of the free base (II) remains in solution. The position of the bromo substituent in II is shown by its reaction as a positive bromine with phenylmagnesium bromide to give bromobenzene.

The bromination of the hydrobromide of I in glacial acetic acid with two equivalents of bromine produces the hydrobromide of 1-methyl-3-carbethoxy-3,5-dibromo-4-piperidone (III).[1] The further addition of bromine in this reaction yields only a perbromide of the salt of III.

When the hydrobromides of II and III are titrated with silver nitrate by the Volhard procedure only the ionic bromine of these salts react. However, titration by the Mohr procedure produces reaction with all of the bromine present in each of these salts. Inasmuch as α-bromo ketones such as the phenacyl bromides do not show any appreciable reaction with silver nitrate in the Mohr titration, it would appear that the reaction of the 5-bromo substituent of III in this titration is *via* an ethyleneimonium bromide of the type postulated to explain a similar behavior of 1-methyl-3-bromo-4-phenyl-1,2,3,6-tetrahydropyridine.[2]

Experimental

1-Methyl-3-bromo-3-carbethoxy-4-piperidone (II) Hydrobromide.—In a 250-ml. 3-necked round-bottom flask equipped with a reflux condenser, glass stirrer and dropping funnel, a solution of 18.5 g. (0.10 mole) of 1-methyl-3-carbethoxy-4-piperidone[3] in 200 ml. of carbon tetrachloride was heated to reflux and 16.0 g. (0.10 mole) of bromine added over a period of twenty minutes. The reaction mixture was heated for an additional fifteen minutes and then allowed to cool. The carbon tetrachloride was decanted and the usual residual oil treated with acetone to cause crystallization of 20.5 g. (58%) of the hydrobromide of II, m. p. 143–145° (dec.).

Anal. Calcd. for $C_9H_{15}Br_2NO_3$: C, 31.33; H, 4.38; Br (1), 23.1; Br (2), 46.2. Found: C, 30.95; H, 4.45; Br (Volhard), 22.7; (Mohr), 46.3.

Bromination of 11.1 g. (0.06 mole) of I in carbon tetrachloride at 0–5° with 4.8 g. (0.03 mole) of bromine yielded 9.2 g. of a precipitate, m. p. 142–146°, which was a mixture of the hydrobromides of I and II (halogen analysis). The filtrate was diluted with an equal volume of ether, and anhydrous hydrogen bromide added to precipitate 7.8 g. of a yellow-orange, hygroscopic solid; after crystallization from acetone, 5.0 g. (48%) of the hydrobromide of II, m. p. 141–143° (dec.), was obtained.

Reaction of 1-Methyl-3-bromo-3-carbethoxy-4-piperidone with Phenylmagnesium Bromide.—A solution of 47.1 g. (0.25 mole) of 1-methyl-3-carbethoxy-4-piperidone (I) in 350 ml. of anhydrous ether was placed in a 500-ml. round-bottom flask equipped with a stirrer and dropping funnel. To this solution was added over a period of fifteen minutes 20.4 g. (0.13 mole) of bromine. The precipitated solid was removed by filtration and the filtrate placed under nitrogen in a 1-l. round-bottom flask equipped with a mercury-seal Hershberg stirrer, reflux condenser and dropping funnel. A solution of 0.13 mole of phenylmagnesium bromide in 150 ml. of ether then was added; the resulting solution was refluxed for eight hours, and then stirred for an additional twelve hours. The reaction mixture was hydrolyzed and neutralized by the slow addition of 145 ml. of 1.04 *N* hydrochloric acid. The aqueous layer was separated and extracted with twenty 50-ml. portions of ether; the ether extracts were combined, dried over anhydrous sodium sulfate and the ether distilled on a steam-bath. The residue was fractionally distilled under reduced pressure to give (a) 9.2 g. bromobenzene, (b) 2.5 g. of I, b. p. 71–75° (1.4 mm.), (c) a residue of 3.7 g.

1-Methyl-3,5-dibromo-3-carbethoxy-4-piperidone (III) Hydrobromide.—In a three-necked 250-ml. round-bottom flask was placed a solution of 10.7 g. (0.04 mole) of 1-methyl-3-carbethoxy-4-piperidone hydrobromide in 100 ml. of glacial acetic acid. The flask was heated in an oil-bath to 65° and 12.8 g. (0.08 mole) of bromine in 15 ml. of glacial acetic acid added over a period of fifteen minutes, after which the heating was continued for one hour. The glacial acetic acid was removed under reduced pressure and the oily residue treated with acetone to precipitate 11 g. (62%) of 1-methyl-3,5-dibromo-3-carbethoxy-4-piperidone hydrobromide, m. p. 153–154° (dec.).

Anal. Calcd. for $C_9H_{14}Br_3NO_3$: C, 25.50; H, 3.33; Br (1), 18.9; Br (3), 56.6. Found: C, 25.54; H, 3.53; Br (Volhard), 18.7; (Mohr), 55.7.

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[1] *Cf.* the bromination of acetoacetic ester, Kharasch, *et al.*, THIS JOURNAL, **59**, 1655 (1937).

[2] McElvain and Safranski, *ibid.*, **72**, 3134 (1950).

[3] McElvain and Rorig, *ibid.*, **70**, 1820 (1948).

Colorimetric Study of Reaction of Siliceous Sodium Silicates with Sodium Hydroxide

BY R. C. MERRILL AND R. W. SPENCER

Changes in the absorption spectrum of the dye pinacyanol chloride in sodium silicate solutions[1,2] have been used to follow their reaction with ammonium sulfate and sulfuric acid.[3] This note shows that color changes of the dye during reactions of the silicates with other substances can be followed by means of an ordinary photoelectric colorimeter equipped with a suitable filter. The data to be presented show differences in silicates of the same composition and concentration but different history, and demonstrate that the re-

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[1] R. C. Merrill, R. W. Spencer and R. Getty, THIS JOURNAL, **70**, 2460 (1948).

[2] R. C. Merrill and R. W. Spencer, *ibid.*, **70**, 3583 (1948).

[3] R. C. Merrill and R. W. Spencer, *ibid.*, **72**, 2894 (1950).

action between the siliceous silicate, $Na_2O \cdot 3.3SiO_2$, and sodium hydroxide is slow. Changes in the electrical conductivity of freshly prepared mixtures of siliceous sodium silicates and sodium hydroxide for as long as ten hours were observed in 1893 by Kohlrausch.[4] Apparently there has been no further published study of the rate of this reaction, which probably involves the breaking down of the micelles present in the more siliceous silicates.

Differences in the colors of dyes in silicate solutions of the same composition and concentration may be large enough to be apparent to the unaided eye. For example, a 1.0×10^{-5} *M* solution of pinacyanol chloride in solutions of crystalline sodium meta- or orthosilicate having the same silica concentration (0.33 *M*) as 0.1 *M* $Na_2O \cdot 3.3SiO_2$ is blue whereas the same concentration of dye in a mixture of 0.1 *M* $Na_2O \cdot 3.3SiO_2$ and sodium hydroxide having exactly the same composition as the meta- or orthosilicate is reddish violet. This difference is due to a different type of silica being present in the solutions rather than to the additional free alkali.[2]

A Klett–Summerson photoelectric colorimeter equipped with an amber filter having maximum transmission at 475 mμ was adjusted to zero density with distilled water in the light path. Density readings were made for 1.0×10^{-5} *M* pinacyanol chloride in sodium metasilicate and sodium orthosilicate solutions containing 0.33 *M* SiO_2 and compared with solutions prepared from $Na_2O \cdot 3.3SiO_2$ and sodium hydroxide to give the same final compositions. The results in the following table show that the addition of sodium hydroxide to a siliceous silicate produces a slow gradual change in the type of silica present.

Final solution	Source	Colorimeter reading 0 hr.	5 hr.	24 hr.
0.33 *M* Na_4SiO_4	Na_4SiO_4	495	...	...
0.33 *M* Na_4SiO_4	$Na_2O \cdot 3.3SiO_2$ + NaOH	330	405	440
0.33 *M* Na_2SiO_3	Na_2SiO_3	460	...	...
0.33 *M* Na_2SiO_3	$Na_2O \cdot 3.3SiO_2$ + NaOH	303	375	395
0.1 *M* $Na_2O \cdot 3.3SiO_2$	$Na_2O \cdot 3.3SiO_2$	264	...	...

The colorimeter reading of the dye in an exceptionally pure sample of sodium metasilicate obtained through the courtesy of Drs. P. Debye and R. V. Nauman of Cornell University was practically the same as in solutions of commercial grade products. Apparently a small amount of impurities does not significantly affect the results.

This method of studying interactions or reactions of colloidal electrolytes by means of their changing metachromatic effect on dyes can probably be used generally. It should be useful in studying the degradation or depolymerization of other molecular colloidal electrolytes, such as pectinic, alginic, and other polyuronic acids, polyacrylic acids and their salts and similar materials.

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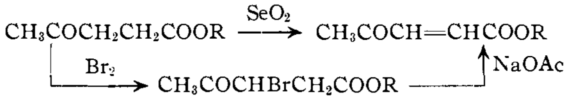
(4) F. Kohlrausch, *Z. physik. Chem.*, **12**, 773 (1893).

The Reaction of Selenium Dioxide with Levulinates

BY SAMUEL RAYMOND

Selenium dioxide has been used to introduce the hydroxyl or carbonyl group into aliphatic compounds at a position adjacent to a keto or other unsaturated group.[1] A second type of selenium dioxide oxidation is the removal of hydrogen forming a double bond.

Levulinic esters are dehydrogenated by selenium dioxide in a reaction of this second type. The products are esters of β-acetylacrylic acid, identical with the esters of this acid synthesized by a known method.[2]



$$CH_3COCH_2CH_2COOR \xrightarrow{SeO_2} CH_3COCH{=}CHCOOR$$

$$CH_3COCH_2CH_2COOR \xrightarrow{Br_2} CH_3COCHBrCH_2COOR \xrightarrow{NaOAc} CH_3COCH{=}CHCOOR$$

Identity was shown by the direct comparison of physical properties, including mixed m. p., and by the preparation of the semicarbazone derivatives. Owing to the low yield and difficulty of separation of the products from the starting materials, this reaction cannot be considered of preparative value for these acetylacrylic esters.

Experimental

One-tenth of a mole of levulinic ester was heated with 0.05 mole of selenium dioxide on a steam-bath. After eighteen hours the precipitated selenium was filtered off and washed with dichloromethane. The filtrate and washings were mixed with 500 ml. of water, saturated with salt, and steam distilled. Two liters of distillate was collected and extracted thoroughly with dichloromethane. The extract was dried and distilled *in vacuo*. The quantity of acetylacrylic ester in the distilled oil was determined from the absorption at 222 mμ. Yields and physical properties are recorded in Table I.

TABLE I

ACETYLACRYLIC ESTERS

Alkyl	Yield, % SeO_2	Wolff	B. p., °C., 15 mm.	Molar extinction log ε	at mμ
Methyl[a]	3.2	34	85–86	4.15	222
Ethyl	3.8	38	93–94[b]	4.00	224
Propyl	9.6	46	103–104	4.04	222
Butyl	13.2	39	118–122	3.98	222
Benzyl	0.0	42	116–120[c]	4.12	222

[a] M.p. 59–60°. [b] Adams and Wilkinson (THIS JOURNAL, **65**, 2207 (1945)) give b.p. 65–67° (2 mm.). [c] At 2 mm.

Methyl acetylacrylate was isolated from the reaction with methyl levulinate by cooling the steam-distilled oil to −20°. The crystals which formed were filtered off and washed with ether–ligroin mixture. Their m.p. was 56–60° and was raised to 59–60° by one recrystallization from ether and ligroin. The mixed m.p. with methyl acetylacrylate prepared by the method of Wolff[2] was unchanged.

The semicarbazones were prepared from the steam-distilled oils by the standard procedure and were recrystallized from dilute alcohol. Although this oil contains a large proportion of levulinic ester the semicarbazones of the acetylacrylates could be isolated easily because they

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(1) For a review see Waitkins and Clark, *Chem. Revs.*, **36**, 241 (1948).

(2) Wolff, *Ann.*, **265**, 229 (1891).